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(54) Title: DETERGENT GRANULE

(57) Abstract

The invention relates to detergent granules of diameter size of from 1.0 mm to 4.5 mm, comprising an acidic source and an alkaline source, capable of reacting together to from a gas.

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Detergent Granule

Technical Field

The present invention relates to a detergent granule having a diameter of from 1.0 mm to 4.5 mm, comprising an acid source and an alkali source, which are suitable for use in laundry washing and dish washing methods. The invention also relates to a process for making the detergent granule.

Background to the Invention

There is a trend amongst commercially available granular detergents manufacturers towards higher bulk densities and towards granular detergent compositions which have a higher content of detergent active ingredients. Such detergents offer greater convenience to the consumer and at the same time reduce the amount of packaging materials which will, ultimately, be disposed of. However, traditional detergent formulations and processes to produce the final detergent powder are not always satisfactory or suitable for these detergents, with higher active ingredient concentration.

Recently, processes have been developed whereby detergent particles or granules can be produced in such a manner that each individual granule or particle has a high content of active ingredients and high density. Examples of such processes are agglomerating and extrusion. However, the agglomerated particles or extruded granules do not always dissolve satisfactory water, due to the increase in their density, the high content of various components, which are partially non-water-soluble, their relatively large particle size (up to 4.5mm).

Therefore, the (high density) detergents, comprising these particles or granules can also have poor solubility properties, leading to a low rate of dissolution, and moreover the formation of gels, and thus to poor dispensing of the product, either from the dispensing drawer of a washing machine, or from a dosing device placed with the laundry inside the machine. Namely, gelling of the detergent is often caused by gelling of particles or granules, which have high content of detergent components, especially high levels of surfactants, upon contact with water. The gel prevents a proportion of the detergent powder from being solubilized in the wash

water which reduces the effectiveness of the powder. This is a particular problem at low water pressures and/or at lower washing temperature.

EP-A-0 639 637 discloses the replacement of perborate bleach with an alkali metal percarbonate to improve the dispensing profile and dissolution rate of a detergent. Citrate or mixtures of citrate with sulphate or carbonate can be used to coat the percarbonate bleach. EP-A-0 639 639 contains a similar disclosure in this respect.

Other ways to improve dispensing include the use of an effervescence system. If the detergent contains an effervescence system then the generation of a gas such as carbon dioxide pushes the particles of the detergent apart, and prevents them from gelling.

The use of effervescence to improve the dispensability of granular materials has been used extensively in pharmaceutical preparations. The most widely used effervescent system in this respect is citric acid in combination with bicarbonate. The use of this simple effervescent system has also been described for improving the dispersibility of pesticidal compositions for controlling water-borne pests, e.g. GB-A-2,184,946.

EP-A-0 534 525 discloses the use of citric acid with a specified particle size range of 350 to 1500 microns.

US -A-5, 114,647 discloses a sanitising composition comprising granules of alkali metal carbonate and aliphatic carboxylic acid of a particle size of 150 to 2,000 microns.

EP-A-0 333 223 discloses a bathing preparation comprising fumaric acid having an average particle size of 50-500 microns.

The Applicants have found that the problem of the poor dispensing of detergent granules of particle size of from 1.0 to 4.5 mm, with a high content of active ingredients, especially a high content of surfactants and especially those detergents with a high density, can be solved or reduced when an acid source and an alkali source is included in the detergent granule. We have found that addition of such an acid source and an alkali source in the detergent granule, improves the solubility and/or dispersion of the active detergent ingredients in the wash water and

eliminates or reduces the problems of fabric or machine damage by solid detergent particles or active ingredients remaining in the washing machine and on washed clothes. It is believed that the acid reacts rapidly with the alkali in the wash water to release the gas. This helps disperse the active detergent ingredients in the particle in general and minimise the formation of high concentrations of ingredients and of insoluble clumps.

The improved dispensing of the detergent granule and the ingredients thereof can amount to an overall improved and more efficient performance.

Furthermore, the detergent or granule residues in the dispensing drawer or dispensing device are reduced.

All documents cited in the present description are, in relevant part, incorporated herein by reference.

Summary of the Invention

According to the present invention there is provided a detergent granule having a diameter of 1.0 to 4.5 mm, comprising an acid source and an alkali source, capable of reacting together in the presence of water to produce a gas. According to the present invention there is also provided a process for making the detergent granule.

Detailed Description of the Invention

Detergent granule

The detergent granule of the present invention has a diameter of 1.0 mm to 4.5 mm and comprises an acid source and an alkali source, capable of reacting together in the presence of water to produce a gas.

More preferably the diameter size of the granule is from 1.3 mm to 2.8 mm, more preferably from 1.3 mm to 2.5 mm, even more preferably from 1.4 mm to 2.1 mm, most preferably from 1.4 mm to 1.8 mm.

The diameter size as defined herein can be determined by sieving a sample of the granules into a number of fractions (typically 5 fractions) on a series of sieves, with mazes of various diameter or aperture size. Granules with a diameter above 4.5 mm will not be used as granules for the present invention. The mean diameter size of the granules can be calculated by plotting the weight fractions, obtained by the sieving, against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

The mean diameter size of the granules of the invention should in a highly preferred embodiment of the invention be such that no more that 3% of particles are greater than 2.5mm, or even 2.1 mm, in diameter and not more than 3% of particles are less than 1.3mm in diameter.

A process for making the granules will be described below.

Components of the granule

Acid Source

In accordance with the present invention, an acid source is present in the detergent granule, capable of reacting with the source of alkali in the presence of water to produce a gas.

In detergent granule, the level of the acid source is preferably of from 0.1% to 50%, more preferably from 0.5% to 25%, even more preferably from 1% to 12%, most preferably from 1% to 7% by weight of the composition.

Preferably, 80% or more of the acid source has a particle size in the range of from about 150 microns to about 710 microns, with at least about 37% by weight of the acid source having a particle size of about 350 microns or less. Preferably, 100% of the acid source has a particle size of no greater than 710 microns. Alternatively, greater than about 38%, more preferably 38.7%, of the acid source has a particle size of about 350 microns or less.

The particle size of the source of acidity is calculated by sieving a sample of the source of acidity on a series of Tyler sieves. For example, a Tyler sieve mesh 100

corresponds to an aperture size of 150 microns. The weight fractions thereby obtained are plotted against the aperture size of the sieves.

The acid source may be any suitable organic, mineral or inorganic acid, or a derivative thereof, or a mixture thereof. The acid source may be a mono-, bi- or tri-protonic acid. Preferred derivatives include a salt or ester of the acid. The source of acidity is preferably non-hygroscopic, which can improve storage stability. However, a monohydrate acid source can be useful herein. Organic acids and their derivatives are preferred. The acid is preferably water-soluble. Suitable acids include citric, glutaric, succinic or adipic acid, monosodium phosphate, sodium hydrogen sulfate, boric acid, or a salt or an ester thereof. Citric acid is especially preferred.

Source of Alkali

In accordance with the present invention the detergent granule comprises an alkali source, which has the capacity to react with the acid source in the presence of water to produce a gas. Preferably this gas is carbon dioxide, and therefore the alkali is a carbonate, or a suitable derivative thereof.

The detergent granule, preferably comprises from about 2% to about 75%, preferably from about 5% to about 60%, most preferably from about 10% to about 30% by weight of the alkali source.

In a preferred embodiment, the alkali source is a carbonate. Examples of preferred carbonates are the alkaline earth and alkali metal carbonates, including sodium carbonate, bicarbonate and sesqui-carbonate and any mixtures thereof with ultra-fine calcium carbonate such as are disclosed in German Patent Application No. 2,321,001 published on November 15, 1973. Alkali metal percarbonate salts may also be included in the detergent compositions and are also suitable sources of carbonate species and are described below in more detail.

Other suitable sources will be known to those skilled in the art.

The alkali source may also comprise other components, such as a silicate. Suitable silicates include the water soluble sodium silicates with an SiO_2: Na_2O ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.0 being preferred, and 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated

salt. Sodium silicate with an SiO_2: Na_2O ratio of 2.0 is the most preferred silicate. Alkali metal persilicates are also suitable sources of alkali herein.

Formation of the granule

The granule of diameter size of 1.0 mm to 4.5 mm can be produced via a variety of methods commonly known. Preferred methods are agglomeration, pre-mixing and spray-on and granulation. The most preferred method for making the granules of the invention is extrusion.

Extruded granules can generally be prepared by mixing the various detergent components, optionally addition of powdered components and/or slip additives, forcing the obtained mixture by pressure through the extruder holes of the required diameter or less, cutting of the extruded paste into extrudates (granules) of the required length and rounding the extrudates. WO 91/13678 and WO 91/02047 describe such processes.

In more detail the extruded granules can be made as follows. The various detergent granule ingredients can be mixed into one paste. Preferably, the various detergent components are pre-mixed in different pastes, preferably two, whereby the acid source preferably is present in a different pre-mixed past than the alkali source, especially when the alkaline source is a carbonate or bicarbonate.

In a highly preferred embodiment, one pre-mixed paste comprises the alkali source and anionic surfactant, and additional components such as zeolite, layered silicate, bleach activator and cationic surfactant, and one pre-mixed paste comprises the acid source and nonionic surfactant. The premixed pastes will then be mixed to form one paste.

Optionally, water and additional detergent components, such as slip additives, bleach, enzymes, bleach activators, stabilisers and soap can be added to the pre-mixed paste or pastes or to the paste as a whole, simultaneously with or shortly after the mixing process has started. Optionally, the bleach activator(s) and enzyme(s) can be dry-added to the finished extrudates or granules.

Preferably the obtained paste is coated with a slip material prior to or simultaneously with the introduction of the paste in the extruder. Under pressure (20 bar or more)

the paste or coated paste is then passed through the holes (of the extruder) of the required diameter or less, whereafter the extruded granules are cut in to granules of the required length (preferably from 0.8 mm to 4.0 mm, more preferably 1.0 mm to 3.0 mm, even more preferably from 1.3 mm to 2.5 mm).

The viscosity of the paste should be controlled to avoid cacking of the paste in the extruder or during mixing and to avoid the paste from blocking the extruder. By constant pressure, the viscosity is best controlled by heating and cooling the paste and/ or the extruder.

Optionally, the obtained granules or extrudates are rounded, to obtain round or spherical granules.

Preferably, the thus obtained granules are dusted with a powder, preferably zeolite, and dried, to form equally shaped granules, and to avoid agglomeration of the granules.

Possible granules, which do not have the required diameter size of 1.0 mm to 4.5 mm, can be removed from the granule mix by sieving.

A variety of compounds are known to be useful herein as slip additives, as mentioned above. Preferred slip additives are those compounds which also have a secondary detergent function, such as certain anionic and nonionic surfactants, polymeric polycarboxylates, polyvinyl alcohols.

A typical agglomeration process involves mixing an effective amount of powder, comprising the alkali and acid source, with a high active component paste, especially high active surfactant, in one or more agglomerators such as a pan agglomerator, a Z-blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV, 29 Chroomstraat 8211 AS, Lelystad, Netherlands, and Gebruder Lodige Maschinenbau GmbH, D-4790 Paderborn 1, Elsenerstrasse 7-9, Postfach 2050, Germany. Most preferably a high shear mixer is used, such as a Lodige CB (Trade Name). The particle size of the resultant agglomerates is controlled within specified limits of 1.0 mm to 4.5 mm.

Optionally, additional detergent ingredients can be sprayed-on an agglomerated particle, having a particle size of just under 1.0 mm to 4.5 mm, to obtain the granule of the present invention.

A high active surfactant paste, as mentioned above, comprising a mix of, typically, from 50% by weight to 95% by weight, preferably 70% by weight to 85% by weight of surfactant, as described hereinafter. The paste may be pumped into the agglomerator at a temperature high enough to maintain a pumpable viscosity, but low enough to avoid degradation of the anionic surfactants used. An operating temperature of the paste of 50°C to 80°C is typical.

Additional components of the granule

The level of the components of the detergent granule can vary, depending on the nature of the granule. The additional components can be detergent ingredients traditionally employed in detergents, such as surfactants, builders, bleaches bleach activators, polymeric compounds, soil release polymers, enzymes, perfumes, suds suppressors, (lime soap) dispersants, soil suspension and anti-redeposition agents, corrosion inhibitors and brightners.

Surfactant

The level of surfactant is preferably from 8% to 60%, more preferably from 10% to 50%, most preferably from 14% to 30% by weight of the granule.

Preferred surfactant are anionic, nonionic and cationic surfactants and mixtures thereof. Preferably, at least one anionic surfactant is present. Preferably, the anionic surfactant is a mixture of anionic sulphate surfactant and anionic sulphonate surfactant, whereof exemples are described below. More preferably one or more nonionic surfactants and anionic surfactants are present. Optionally, ampholytic, amphoteric and zwitterionic surfactants can be present in the particle

A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of

suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Anionic surfactant

The detergent granule in accord with the present invention preferably comprise one or more anionic surfactants. Essentially any anionic surfactants useful for detersive purposes can be comprised in the detergent composition. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono- di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

The level of anionic surfactant is preferably from 2% to 40%, more preferably from 4% to 30%, even more preferably from 5% to 25%, most preferably from 6% to 15% by weight of the granule.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic sulfate surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C_5-C_{17} acyl-N-(C_1-C_4 alkyl) and -N-(C_1-C_2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl sulfate surfactants are preferably selected from the linear and branched primary C_{10}-C_{18} alkyl sulfates, more preferably the C_{11}-C_{15} branched chain alkyl sulfates and the C_{12}-C_{14} linear chain alkyl sulfates.

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C_{10}-C_{18} alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C_{11}-C_{18}, most preferably C_{11}-C_{15} alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C_5-C_{20} linear alkylbenzene sulfonates, alkyl ester sulfonates, C_6-C_{22} primary or secondary alkane sulfonates, C_6-C_{24} olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula $RO(CH_2CH_20)_x$ $CH_2C00^-M^+$ wherein R is a C_6 to C_{18} alkyl group, x ranges from O to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula $RO-(CHR_1-CHR_2-O)-R_3$ wherein R is a C_6 to C_{18} alkyl group, x is from 1 to 25, R_1 and R_2 are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R_3 is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants

for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

Alkali metal sarcosinate surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula R-CON (R^1) CH_2 COOM, wherein R is a C_5-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Cationic surfactants

Another preferred surfactant of the invention is one or more cationic surfactants. Suitable cationic surfactants include the quaternary ammonium surfactants selected from mono C_6-C_{16}, preferably C_6-C_{10} N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups. Another preferred cationic surfactant is an C_6-C_{18} alkyl or alkenyl ester of an quaternary ammonium alcohol, such as quaternary choline esters.

The level of cationic surfactant is preferably from 0.2% to 20%, more preferably from 0.5% to 15%, even more preferably from 1% to 10%, most preferably from 1% to 5% by weight of the granule.

Nonionic surfactant

The detergent granule of the present invention preferably contains a nonionic surfactant. Essentially any nonionic surfactant can be used herein.

The level of nonionic surfactant is preferably from 1% to 30%, more preferably from 2% to 25%, even more preferably from 3% to 15%, most preferably from 4% to 12% by weight of the granule.

Alkoxylated nonionic surfactant

Essentially any alkoxylated nonionic surfactants are suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

Preferred alkoxylated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

Nonionic alkoxylated alcohol surfactant

The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein : R1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable C1-C4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R_2 is a C_5-C_{31} hydrocarbyl, preferably straight-chain C_5-C_{19} alkyl or alkenyl, more preferably straight-chain C_9-C_{17} alkyl or alkenyl, most preferably straight-chain C_{11}-C_{17} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

Nonionic fatty acid amide surfactant

Suitable fatty acid amide surfactants include those having the formula: $R^6CON(R^7)_2$ wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen,

C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, and $-(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

Nonionic alkylpolysaccharide surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units.

Preferred alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)t(glycosyl)_x$$

wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

Optional surfactants

Amphoteric surfactant

Optional amphoteric surfactants for use in the detergent granule include the amine oxide surfactants and the alkyl amphocarboxylic acids.

Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C_{10}-C_{18} alkyl dimethylamine oxide, and C_{10-18} acylamido alkyl dimethylamine oxide.

A suitable example of an alkyl aphodicarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic surfactant

Optionally, zwitterionic surfactants can be incorporated into the detergent granule. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Suitable betaines are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C_6-C_{18} hydrocarbyl group, each R^1 is typically C_1-C_3 alkyl, and R^2 is a C_1-C_5 hydrocarbyl group. Preferred betaines are C_{12-18} dimethyl-ammonio hexanoate and the C_{10-18} acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Water-soluble builder compound

The detergent granule of the present invention can contain a water-soluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the granule.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more that two carbon atoms, borates, phosphates, and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric

acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

Suitable examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

Partially soluble or insoluble builder compound

The detergent granuleof the present invention may contain a partially soluble or insoluble builder compound, typically present at a level of from 1% to 80% by

weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the granule.

Examples of largely water insoluble builders include the sodium aluminosilicates.

Suitable aluminosilicate zeolites have the unit cell formula $Na_z[(AlO_2)_z(SiO_2)y]$. xH_2O wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula

$$Na_{12}[AlO_2)_{12}(SiO_2)_{12}].\ xH_2O$$

wherein x is from 20 to 30, especially 27. Zeolite X has the formula $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}].\ 276\ H_2O$.

Preferred crystalline layered silicates for use herein have the general formula

$$NaMSi_xO_{2x+1}.yH_2O$$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. Herein, x in the general formula above preferably has a value of 2, 3 or 4 and is preferably 2. The most preferred material is δ-$Na_2Si_2O_5$, available from Hoechst AG as NaSKS-6.

Perhydrate bleach components

Perborate component

A preferred perhydrate bleach for use in the detergent granule of the present invention is a perborate component.

The perborate is preferably present at a level of from 1% to 40% by weight, more preferably from 6% to 25% by weight, most preferably from 13% to 20% by weight of the granule.

The perborate is preferably in the form of a salt, normally in the form of the alkali metal, preferably sodium salt.

The perborate bleach is preferably a sodium perborate in the form of the monohydrate or tetrahydrate, respectively of nominal formula $NaBO_2H_2O_2$ and $NaBO_2H_2O_2.3H_2O$.

The perborate bleach may be included as the crystalline solid without additional protection. However, preferred executions of certain granular compositions utilize a coated form of the perborate bleach which provides better storage stability for the perhydrate salt in the granular product. Suitable coatings comprise inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as waxes, oils, or fatty soaps.

Other perhydrate bleaches are for example a metal percarbonates, particularly sodium percarbonate. Sodium percarbonate is an addition compound having a formula corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid.

Potassium peroxymonopersulfate is another optinal inorganic perhydrate salt of use in the detergent granules herein.

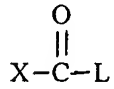
Organic peroxyacid bleaching system

A preferred feature of detergent granules of the invention is an organic peroxyacid bleaching system. In one preferred execution the bleaching system contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches, such as the perborate bleach of the

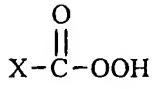
claimed invention. In an alternative preferred execution a preformed organic peroxyacid is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

Peroxyacid bleach precursor

Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as



where L is a leaving group and X is essentially any functionality, such that on perhydroloysis the structure of the peroxyacid produced is



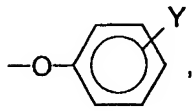
Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the detergent granule.

Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Leaving groups

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from the group consisting of: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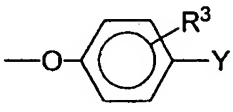
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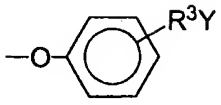

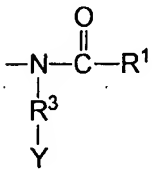
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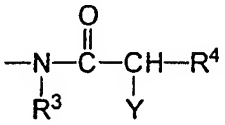
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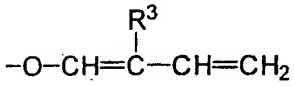
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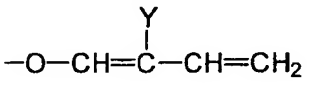
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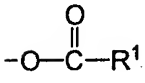
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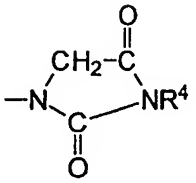
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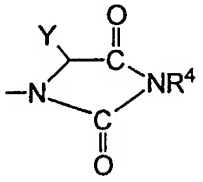
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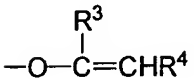
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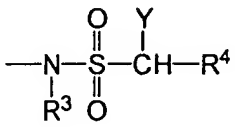


and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3, and Y is H or a solubilizing group. Any of R^1, R^3 and R^4 may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammmonium groups.

The preferred solubilizing groups are $-SO_3^-M^+$, $-CO_2^-M^+$, $-SO_4^-M^+$, $-N^+(R^3)_4X^-$ and $O<--N(R^3)_3$ and most preferably $-SO_3^-M^+$ and $-CO_2^-M^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

Alkyl percarboxylic acid bleach precursors

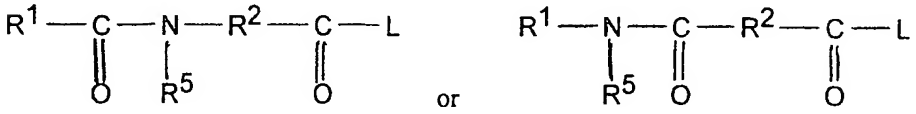
Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis.

Preferred alkyl percarboxylic precursor compounds of the imide type include the N-,N,N^{1}N^1 tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose.

Amide substituted alkyl peroxyacid precursors

Amide substituted alkyl peroxyacid precursor compounds are suitable herein, including those of the following general formulae:



wherein R^1 is an alkyl group with from 1 to 14 carbon atoms, R^2 is an alkylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl group

containing 1 to 10 carbon atoms and L can be essentially any leaving group. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Perbenzoic acid precursor

Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis. Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, and the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, and those of the imide type including N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole. Other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Cationic peroxyacid precursors

Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammmonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically present in the solid detergent compositions as a salt with a suitable anion, such as a halide ion.

The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter.

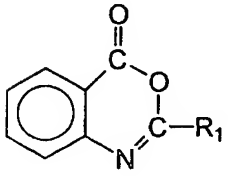
Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams and the trialkyl ammonium methylene alkyl caprolactams.

Benzoxazin organic peroxyacid precursors

Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:

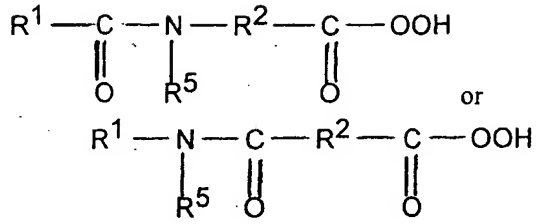


wherein R_1 is H, alkyl, alkaryl, aryl, or arylalkyl.

Preformed organic peroxyacid

The organic peroxyacid bleaching system may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid , typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the granule.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



or

wherein R^1 is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioc acid, diperoxytetradecanedioc acid and diperoxyhexadecanedioc acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also suitable herein.

Heavy metal ion sequestrant

The granule of the present invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the granule.

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminotetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β-alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N-N'-diglutaric acid (EDDG) and 2-hydroxypropylenediamine-N-N'-disuccinic acid (HPDDS) are also suitable.

Enzyme

Another preferred ingredient useful in the detergent granules of the invention is one or more additional enzymes.

Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries

A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α-amylases obtained from a special strain of B licheniformis, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the granule.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the granule.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

Organic polymeric compound

Organic polymeric compounds are preferred additional components of the granule, and are preferably present as components of any particulate components where they may act such as to bind the particulate component together. By organic polymeric compound it is meant herein essentially any polymeric organic compound

commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions, including any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein.

Organic polymeric compound is typically incorporated in the detergent granules of the invention at a level of from 0.1% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the granule.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 100,000, especially 40,000 to 80,000.

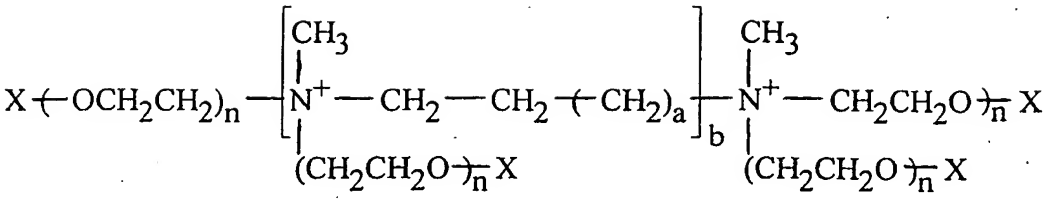
The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

Another organic compound, which is a preferred clay dispersant/ anti-redeposition agent, for use herein, can be the ethoxylated cationic monoamines and diamines of the formula:



wherein X is a nonionic group selected from the group consisting of H, C_1-C_4 alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof, a is from 0 to 20, preferably from 0 to 4 (e.g. ethylene, propylene, hexamethylene) b is 1 or 0; for cationic monoamines (b=0), n is at least 16, with a typical range of from 20 to 35; for cationic diamines (b=1), n is at least about 12 with a typical range of from about 12 to about 42.

Other dispersants/ anti-redeposition agents for use herein are described in EP-B-011965 and US 4,659,802 and US 4,664,848.

Suds suppressing system

The detergent granules, when formulated for use in machine washing compositions, preferably comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the granule.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alcanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone

antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C_{18}-C_{40} ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

A preferred suds suppressing system comprises

(a) antifoam compound, preferably silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination

(i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and

(ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound;

wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;

(b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to

10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544;

(c) an inert carrier fluid compound, most preferably comprising a C_{16}-C_{18} ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

Clay softening system

The granule may contain a clay softening system comprising a clay mineral compound and optionally a clay flocculating agent.

The clay mineral compound is preferably a smectite clay compound. Smectite clays are disclosed in the US Patents Nos. 3,862,058, 3,948,790, 3,954,632 and 4,062,647. European Patents Nos. EP-A-299,575 and EP-A-313,146 in the name of the Procter and Gamble Company describe suitable organic polymeric clay flocculating agents.

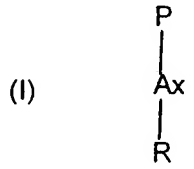
Polymeric dye transfer inhibiting agents

The detergent granules may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

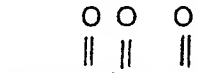
The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidonepolymers or combinations thereof.

a) Polyamine N-oxide polymers

Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :



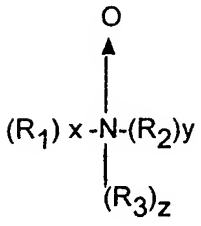
wherein P is a polymerisable unit, and



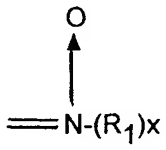
A is NC, CO, C, -O-, -S-, -N-; x is O or 1;

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



or



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from

aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyrridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit. A preferred class of these polyamine N-oxides comprises the polyamine N-oxides having the general formula (I) wherein R is an aromatic,heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.

The polyamine N-oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

Suitable herein are coploymers of N-vinylimidazole and N-vinylpyrrolidone having an average molecular weight range of from 5,000 to 50,000. The preferred copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2.

c) Polyvinylpyrrolidone

The detergent granules herein may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000. Suitable polyvinylpyrrolidones are commercially valuable from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

d) Polyvinyloxazolidone

The detergent granules herein may also utilize polyvinyloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinyloxazolidones have an average molecular weight of from 2,500 to 400,000.

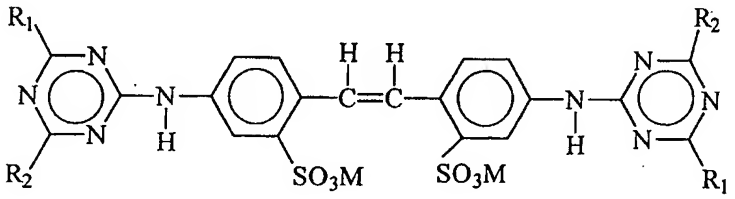
e) Polyvinylimidazole

The detergent granules herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000.

Optical brightener

The detergent granules herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners.

Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename

Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Cationic fabric softening agents

Cationic fabric softening agents can also be incorporated into the detergent granules. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

Cationic fabric softening agents are typically incorporated at total levels of from 0.5% to 15% by weight, normally from 1% to 5% by weight.

Other optional ingredients

Other optional ingredients suitable for inclusion in the particle and the detergent compositions include perfumes, colours and filler salts, with sodium chloride and sulfate being a preferred filler salt.

Density

The bulk density of granules is typically of at least 650 g/litre, more preferably from 850 g/litre to 1200 g/litre. Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm high and has internal diameters of 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement eg; a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide a bulk density in g/litre. Replicate measurements are made as required.

The composition is preferably soluble in cold or cool water, i.e. the composition readily dissolves/disperses in water at a temperature between about 0°C and 32.2°C, preferably between about 1.6°C and 10°C.

Laundry washing method

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent granules in accord with the invention. By an effective amount of the detergent granules it is meant from 40g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

In a preferred use aspect a dispensing device is employed in the washing method. The dispensing device is charged with the detergent product, and is used to introduce the product directly into the drum of the washing machine before the commencement of the wash cycle. Its volume capacity should be such as to be able to contain sufficient detergent product as would normally be used in the washing method.

Once the washing machine has been loaded with laundry the dispensing device containing the detergent product is placed inside the drum. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its contact with the wash water.

To allow for release of the detergent product during the wash the device may possess a number of openings through which the product may pass. Alternatively, the device may be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the detergent product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the washing machine at this stage of the wash cycle.

Preferred dispensing devices are reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle. Especially preferred dispensing devices for use with the composition of the invention have been described in the following patents; GB-B-2, 157, 717, GB-B-2, 157, 718, EP-A-0201376, EP-A-0288345 and EP-A-0288346. An article by J.Bland published in Manufacturing Chemist, November 1989, pages 41-46 also describes especially preferred dispensing devices for use with granular laundry products which are of a type commonly know as the "granulette". Another preferred dispensing device for use with the compositions of this invention is disclosed in PCT Patent Application No. WO94/11562.

Especially preferred dispensing devices are disclosed in European Patent Application Publication Nos. 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing process. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

Alternatively, the dispensing device may be a flexible container, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in European published Patent Application No. 0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European published Patent Application Nos. 0011500, 0011501, 0011502, and 0011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

Packaging for the compositions

Commercially marketed executions of the bleaching compositions can be packaged in any suitable container including those constructed from paper, cardboard, plastic materials and any suitable laminates. A preferred packaging execution is described in European Application No. 94921505.7.

Abbreviations used in following Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

LAS	:	Sodium linear C_{12} alkyl benzene sulfonate
TAS	:	Sodium tallow alkyl sulfate
C45AS	:	Sodium C_{14}-C_{15} linear alkyl sulfate
CxyEzS	:	Sodium C_{1x}-C_{1y} branched alkyl sulfate condensed with z moles of ethylene oxide
C45E7	:	A C_{14-15} predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
C25E3	:	A C_{12-15} branched primary alcohol condensed with an average of 3 moles of ethylene oxide
C25E5	:	A C_{12-15} branched primary alcohol condensed with an average of 5 moles of ethylene oxide
CEQ	:	$R_1COOCH_2CH_2.N^+(CH_3)_3$ with $R_1 = C_{11}$-C_{13}
QAS	:	$R_2.N^+(CH_3)_2(C_2H_4OH)$ with $R_2 = C_{12}$ - C_{14}
Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut oils.
TFAA	:	C_{16}-C_{18} alkyl N-methyl glucamide
TPKFA	:	C12-C14 topped whole cut fatty acids
STPP	:	Anhydrous sodium tripolyphosphate
Zeolite A	:	Hydrated Sodium Aluminosilicate of formula $Na_{12}(AlO_2SiO_2)_{12}.27H_2O$ having a primary particle size in the range from 0.1 to 10 micrometers
NaSKS-6	:	Crystalline layered silicate of formula δ -$Na_2Si_2O_5$
Citric acid	:	Anhydrous citric acid

	Carbonate	:	Anhydrous sodium carbonate with a particle size between 200 μm and 900μm
	Bicarbonate	:	Anhydrous sodium bicarbonate with a particle size distribution between 400μm and 1200μm
	Silicate	:	Amorphous Sodium Silicate (SiO_2:Na_2O; 2.0 ratio)
	Sodium sulfate	:	Anhydrous sodium sulfate
	Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425μm and 850μm
	MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
	CMC	:	Sodium carboxymethyl cellulose
	Protease	:	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
	Alcalase	:	Proteolytic enzyme of activity 3AU/g sold by NOVO Industries A/S
	Cellulase	:	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
	Amylase	:	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
	Lipase	:	Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
	Endolase	:	Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
	PB4	:	Sodium perborate tetrahydrate of nominal formula $NaBO_2.3H_2O.H_2O_2$
	PB1	:	Anhydrous sodium perborate monohydrate bleach of nominal formula $NaBO_2.H_2O_2$
	Percarbonate	:	Sodium Percarbonate of nominal formula $2Na_2CO_3.3H_2O_2$
	NOBS	:	Nonanoyloxybenzene sulfonate in the form of the sodium salt.
	TAED	:	Tetraacetylethylenediamine

DTPMP :		Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060
Photoactivated	:	Sulfonated Zinc Phthlocyanine encapsulated in bleach dextrin soluble polymer
Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.
HEDP	:	1,1-hydroxyethane diphosphonic acid
PVNO	:	Polyvinylpyridine N-oxide
PVPVI	:	Copolymer of polyvinylpyrolidone and vinylimidazole
SRP 1	:	Sulfobenzoyl end capped esters with oxyethylene oxy and terephtaloyl backbone
SRP 2	:	Diethoxylated poly (1, 2 propylene terephtalate) short block polymer
Silicone antifoam :		Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.

In the following Examples all levels are quoted as % by weight of the composition:

Example 1

The following laundry detergent granules A to F were prepared in accord with the invention:

	A	B	C	D	E	F
TAS	8.5	3.5	5.5	8.0	6.8	7.6
LAS	6.0	7.0	6.2	8.0	6.8	7.0
C25E3	4.4	6.7	6.5	5.8	6.0	5.4
citrate	1.0	0.5	-	0.7	0.4	0.8

Zeolite A	18.1	18.1	26.0	15.0	24.0	10.5
Carbonate	9.0	12.0	13.0	17.0	8.5	7.0
Citric acid	3.4	1.4	1.4	0.5	5.0	0.8
Silicate	8.1	5.1	6.1	12.0	15.0	18.0
Sodium sulfate	1.0	-	2.0	2.4	-	-
PB1	9.0	10.0	9.0	12.0	8.0	13.0
PB4	5.5	7.0	1.5	4.5	3.5	2.5
TAED	0.3	0.2	-	0.5	0.5	0.5
HEDP	4.3	5.3	1.5	0.6	1.8	0.4
MA/AA	0.2	0.2	2.5	0.9	1.1	0.2
CMC	1.0	0.4	0.5	0.2	1.2	1.6
amylase	0.3	0.4	0.6	1.1	1.0	0.1
cellulase	-	0.3	0.5	-	0.2	-
lipase	1.0	2.0		0.5	3.0	2.5
protease	0.3	0.3	0.3	0.3	0.3	0.3
Perfume	0.5	0.2	0.3	0.2	0.5	0.5
Silicone antifoam						
Misc/minors to 100%						
	850	850	850	850	850	850
Density in g/litre						

Example 2

The following laundry detergent granules G to L were prepared in accord with the invention:

	G	H	I	J	K	L
Paste I						
TAS	4.5	-	5.5	8.0	6.8	7.6
LAS	8.0	12.0	6.2	8.0	6.8	7.0
citric acid	2.0	4.0	7.0	0.5	0.8	1.0
citrate	1.0	0.5	-	0.7	0.4	0.8
Zeolite A	18.1	18.1	26.0	15.0	24.0	10.0
HEDP	0.3	0.2	0.9	-	0.5	-
MA/AA	4.3	5.0	6.5	5.8	3.0	-
CMC	0.2	0.4	0.9	1.0	2.5	3.0
Paste II						
C25E3	5.5	3.5	7.5	8.7	4.5	2.0
Carbonate	6.9	15.3	17.9	21.0	11.0	13.0
Silicate	3.4	1.4	1.4	4.5.	5.0	3.0
Sodium sulfate	8.1	5.1	6.1	12.0	15.0	18.0
additives						

PB1	1.0	-	2.0	2.4	-	-
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.2	0.3	0.2	0.5	0.5
PB4	9.0	10.0	3.0	12.0	5.0	13.0
dry added						
amylase	1.0	0.4	0.5	0.2	-	-
cellulase	0.3	0.4	0.6	1.1	1.0	-
lipase	-	0.3	0.5	-	0.2	-
protease	1.0	2.0		0.5	3.0	2.5
TAED	5.5	7.0	1.5	4.5	3.5	8.5
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	650

Example 3

The following granular laundry detergent compositions were prepared in accord with the invention:

	M	N	O	p
LAS	5.61	4.76	7.5	8.5
TAS	1.86	1.57	3.5	1.4
C45AS	2.24	3.89	2.2	3.5
C25AE3S	0.76	1.18	1.1	1.1
C45E7	-	5.0	4.0	-
C25E3	5.5	-	-	3.0
CEQ	2.0	2.0	-	-
QAS	-	-	-	1.0
STPP	-	-	-	-
Zeolite A	19.5	19.5	19.5	16.5
NaSKS-6/citric acid (79:21)	10.6	10.6	10.6	10.6
Carbonate	21.4	21.4	16.4	18.2
Bicarbonate	2.0	2.0	2.0	-
Silicate	-	-	-	3.0
Sodium sulfate	-	14.3	-	-
PB4	13.7	15.0	14.0	17.5
TAED	3.1	-	4.2	-

DETPMP	0.2	0.2	0.2	0.2
HEDP	0.3	0.3	0.3	0.3
Protease	0.85	0.85	0.85	0.85
Lipase	0.15	0.15	0.15	0.15
Cellulase	0.28	0.28	0.28	0.28
Amylase	0.1	0.1	0.1	-.1
MA/AA	1.6	1.6	1.6	1.6
CMC	0.4	0.4	0.4	0.4
Photoactivated bleach (ppm)	27 ppm	27 ppm	27 ppm	27 ppm
Brightener 1	0.19	0.19	0.19	0.19
Brightener 2	0.04	0.04	0.04	0.04
Perfume	0.3	0.3	0.3	0.3
Silicone antifoam	2.4	2.4	2.4	2.4
Citric acid	1.5	3.5	4.0	4.5
Minors/misc to 100%				

WHAT IS CLAIMED IS:

1. A detergent granule having a diameter size of from 1.0mm to 4.5mm, comprising an acid source and an alkali source wherein said acid source and alkali source are capable of reacting together in the presence of water to produce a gas.

2. A detergent granule according to claim 1 wherein said acid source is present at a level of 0.5% to 25% by weight of the granule.

3. A detergent granule according to claim 1 or 2 wherein said acid source is present at a level of 1% to 12% by weight of the granule.

4 A detergent granule according to any proceeding claim wherein said alkali source is present at a level of 5% to 60% by weight of the granule.

5. A detergent granule according to any preceding claim wherein said alkali source comprises an alkaline salt selected from an alkali metal or alkaline earth metal carbonate, bicarbonate or sesqui-carbonate.

6. A detergent granule according to any proceeding claim wherein said acid source comprises an organic acid.

7. A detergent granule according to any preceding claim wherein the acid source is a citric acid.

8. A detergent granule according to any preceding claim wherein the diameter of the granule is from 1.3 mm to 2.5 mm.

9. A detergent granule according to any preceding claim wherein 100% of the acid source has a particle size of no greater than 710 microns.

10. A detergent granule according to any preceding claim, comprising from 10% to 50% by weight surfactant, including anionic and/ or nonionic surfactant.

11. A detergent composition according to Claim 10 wherein said anionic surfactant is a mixture of anionic sulphate surfactant and anionic sulphonate surfactant.

12. A detergent granule according to any preceding claim wherein a perborate component is present.

13. A process for making the detergent granule according to any of claims 1 to 8 by extrusion, the process comprising forcing a paste, comprising the acid source and the alkali source, under pressure through holes of an extruder, said holes having a diameter of 1.0 mm to 4.5 mm, whereafter the extruded paste is cut into granules.

14. A process according to claim 13 whereby said paste comprises at least two pre-mixed pastes, comprising a first pre-mixed paste which comprises the acid source and a second pre-mixed paste which comprises the alkali source.

15. A method of washing laundry in a domestic washing machine comprising, introducing into a dispensing device which is placed in the drum of the washing machine, or introducing into the dispensing drawer of a washing machine, an effective amount of a detergent granule of any one of claims 1 to 12

INTERNATIONAL SEARCH REPORT

Int: ional Application No
PCT/IB 98/00357

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/00 C11D3/10 C11D3/20

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CH 659 082 A (CIBA GEIGY AG) 31 December 1986 see page 3, column 3, lines 45,46; page 3, column 2, line 1; page 4, column 2, line 25 - page 5, column 1, line 34; examples 1,2,14-17; claims 1-10	1-15
X	US 4 252 664 A (INAMORATO JACK T) 24 February 1981 see column 4, line 42 - line 51; claim 1	1,3,9
X	US 3 769 224 A (INAMORATO J) 30 October 1973 see column 4, line 28 - line 36; claim 1	1,3,9

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 June 1998	06/07/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Ainscow, J

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INTERNATIONAL SEARCH REPORT

Intl onal Application No
PCT/IB 98/00357

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO 91 13678 A (HENKEL KGAA) 19 September 1991 cited in the application see page 8, line 27 - page 9, line 3; claims 1-23; figures 1-11; examples 1-9	13,14
A	WO 91 02047 A (HENKEL KGAA) 21 February 1991 cited in the application see page 10, line 28 - page 1, line 6; page 14, lines 5-24; claims 1-11; examples 1-10	13,14

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int ional Application No
PCT/IB 98/00357

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